

[illegible]

KRICHEVSKIY, I. P.

184T17

USSR/Chemistry - Compressed Gases 21 Jun 51

"Method of Determining Compressibility of Gases at High Pressures," I. P. Krichevskiy, D. S. Tsiklis, State Sci Res and Plan Inst of Nitrogen Ind

"Dok Ak Nauk SSSR" Vol LXXVIII, No 6, pp 1169-1172

In detg compressibility of gases in steel vessels by applying elevated pressure on one side, it is difficult to est elastic and plastic deformation of vessel. Method described eliminates this fault by using newly designed app

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USSR/Chemistry - Compressed Gases 21 Jun 51  
(Contd)

which has gasket instead of ordinary seal for the piston. Compression of gas proceeds under displacement of mercury into piezometer by liquid transmitting pressure. Tested method by compressing  $H_2$  at 500 to 3,000-6,000 at.

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KRICHEVSKIY, I.R.

PHASE I Treasure Island Bibliographic Report

BOOK

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Call No.: QD501.K846 1952

Author: KRICHEVSKIY, I.R.

Full Title: PHASE EQUILIBRIUMS IN SOLUTIONS AT HIGH PRESSURES, 2nd edition

Transliterated Title: Fazovye ravnovesiya v rastvorakh pri vysokikh davleniyakh

Publishing Data

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FRICHEVSKIY, I.R.

00000070

Card 2/2

Call No. QD501.KB46 1952

Full Title: PHASE EQUILIBRIUMS IN SOLUTIONS AT HIGH PRESSURES, 2nd edition

Text Data

Coverage: The monograph summarizes the results of research on phase equilibria in solutions at high pressures. Particular emphasis is placed on problems in which gas is one of the balancing coexistent phases. 62 Diagrams.

Purpose: A work for university instructors, research workers, and industrial personnel interested in problems of phase equilibria.

Facilities: None.

No. of Russian References: References listed at end of each chapter.

Available: Library of Congress.

KRICHEVSKIY, I. R.

Phase and volume relations in liquid-gas systems at high pressures. IV. I. R. Krichevskii and G. D. Efremova. *Zhur. Fiz. Khim.* 26, 1117-21 (1952); cf. *C.A.* 46, 48908. The vol. and phase relations were studied at 25-50° and at 100-800 atm. for the N-liquid NH<sub>3</sub> system and at 25-50° and 100-800 atm. for the H-liquid NH<sub>3</sub> system. The sol. and the partial molar vol. of N and H in liquid NH<sub>3</sub> were detd. These systems obey the equations for dil. non-electrolytes. The const. for these equations, Henry coeff., was detd. by least squares. J. Rovtar Leach

CA

Shape of the boundary curve near the critical point I. R. Krichevskii. *Doklady Akad. Nauk S.S.S.R.* 83, 435-8 (1952) -- Thermodynamic analysis shows that on passing from the homogeneous to the heterogeneous region through the crit. phase there is a discontinuous jump  $\Delta C_p$  of the heat capacity  $C_p$  at the crit. point, defined by  $\lim_{N_1 \rightarrow N_{1c}} \Delta C_p =$

$$-(\partial^2 H / \partial N_1^2)_{p, T, c} \lim_{N_1 \rightarrow N_{1c}} (N_{1c} - N_1) (\partial N_1 / \partial T)_{p, c},$$

where  $N$  = mole fraction,  $H$  = heat content, and  $c$  is the index of the crit. phase. This discontinuity is finite if the boundary curve  $T, N_1$  in the vicinity of the crit. point is a parabola; if it is flatter,  $\Delta C_p$  is infinite. In all cases, the discontinuity is pos. Similarly, there is a discontinuity  $\Delta \alpha$  of the deriv.  $(\partial \tau / \partial T)_{p, c}$ , where  $\tau$  = mol. vol. The equation of the crit. curve is  $(dp/dT)_c = (1/T)[(\partial^2 H / \partial N_1^2)_{p, T} (\partial \tau / \partial N_1)_{p, T}]$ , which can also be written in the form  $(dp/dT)_c = (1/T)(\Delta C_p / \Delta \alpha)$ . This equation is only formally analogous to Ehrenfest's (C.A. 27, 5215) equation of the curve of phase transitions of the 2nd kind. N. Thon

KRICHEVSKIY, I. R.

U S S R .

Phase and volume correlations in liquid-gas systems at high pressures. V. The ammonia-methane system. I. R. Krichevskiy and G. D. Litvinov. Zhur. Fiz. Khim. 27, 1682-1683 (1953). C. C. A. 49, 2838. The solubility of methane (I) in liquid NH<sub>3</sub> (II), the solv. of II in I and the molar vols. of unsatd. solns. of II in I were found at 25 and 40° under pressures from 1 to 775 atm. Data calculated, as are the partial molar vols. of I dissolved in II ( $\bar{v}_1$ ); the Henry coeffs. for the latter at 25 and 40° are 2170 and 1910 atm. per unit mole fraction, resp. These values are in accord with those calcd. by means of the equation

$$RT \ln(f_1/N_1) = RT \ln K(p^*, T) + \int_0^p (\bar{v}_1 - A) dp,$$

where  $f_1$ ,  $N_1$ ,  $K(p^*, T)$ , and  $A$  are volatility of dissolved I, mole fraction of the latter, Henry coeff. for vapor pressure of satd. II, and a const. equal to 165,600 and 117,000 cm.<sup>3</sup>/atm. at 25 and 40°, resp. J. W. Lowenberg, Jr.

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KRICHEVSKIY, I. R.

✓ The form of the boundary curve for the system phenol-water near the critical point. I. R. Krichevskiy, N. E. Kharanova, and L. R. Levinzon. *Dokl. Akad. Nauk S.S.S.R.* 94, 509-12 (1954). -- By means of a novel dilatometer with built-in stirrer the sp. vol. of the system phenol-water was investigated, in both the homogeneous and heterogeneous states, for various mixts. For the mixts. with 14.80 and 15.25 wt. % phenol there is a discontinuity in the slope of the graph of sp. vol. vs. temp., at about 58°, amounting to  $-4 \times 10^{-4}$  cc./degree g.; for 55.15 and 55.45%, 60°,  $+6 \times 10^{-4}$ ; 49.20% (no temp. given),  $+4 \times 10^{-4}$ ; 21.20 and 31.80%, none discernible. The limits of accuracy are about  $\pm 1 \times 10^{-4}$ . Calens. that assume the curve to be a parabola, and that use standard thermodynamic equations and other literature data, give a value of  $1.5 \times 10^{-4}$  for  $(\partial v / \partial T)_{p,c} - (\partial v / \partial T)_{p,h}$ , where the partial or sp. vol. is at const. pressure, const. concn. of solute, and at the crit. point. This agrees with the above exptl. figure within exptl. error. The conclusion is that this min. in the size of the discontinuity at or near the crit. point (and all other facts on the system phenol-water) fits the classical theory for crit. phenomena. This is contrary to the theory of Semchenko (C.A. 49, 7352e), which assumes a max. in the value of the discontinuity for both sp. vol. and sp. heat at the crit. point.

R. T. Mvera

(7)



USSR/Chemistry - Physical chemistry

Card 1/1 Pub. 22 - 30/47

Authors : Krichewskiy, I. R.; Khazanova, N. E.; and Linshits, L. R.

Title : Diffusion in a binary liquid system in the critical zone

Periodical : Dok. AN SSSR 99/1, 113-116, Nov 1, 1954

Abstract : Experiments showed that complete discontinuation of diffusion in a binary liquid system close to its critical point has a great effect on the nature of the processes connected with the transfer of the substance. It was established that the chemical reaction over a heterogeneous catalyst must occur in the diffusion zone when the binary system is close to the critical zone. The rate of absorption of the substance from its binary solution was found to be zero when reaching the critical zone. The role of other critical phenomena on the kinetics of the reaction processes, is explained. Nine references: 5-USSR; 2-USA; 1-English and 1-French (1903-1954). Table; drawing.

Institution : State Scientific-Research and Planning Institute of the Nitrogen Industry

Presented by: Academician A. N. Frumkin, June 22, 1954

KRICHEVSKIY, L.L.

KRICHEVSKIY, I.R.; KHAZANOVA, N.Ye.; LINSHITS, L.R.

Dilatometry of binary liquid systems in the critical region.  
Zhur.fiz.khim. 29 no.3:547-557 Mr '55. (MLRA 8:7)  
(Dilatometry) (Systems (Chemistry)) (Liquids)

KRICHEVSKIY, I. R.

Critical phenomena I. R. Krichevskiy and N. E. Khazanova. *Zhur. Fiz. Khim.* 36, 1837 (1962).

The classical theory of crit. phenomena requires a confirmation of a no. of points: that the crit. point is actually a point, and not a range of states; that it is the end point of a 2-phase equil., in which the existing conditions become identical; the shape of the boundary curve, and the crit. isotherm near the crit. point remain to be accurately defined. The classical thermodynamic statements were derived from assumptions, the accuracy of which must be confirmed experimentally. The reasons for doubting these assumptions are the neglect of the surface forces and an absence of math. characteristics of the crit. points. These questions could be solved in a pers. way by using a new investigation method of studying discontinuities in some of the properties of the system at the intersection of the boundary curves at the crit. point. Equations connecting the size with the shape of the boundary curve were derived on the assumption that the crit. point cannot be expressed mathematically, and that even a strongly developed surface of demarcation between the existing phases is not reflected in their thermodynamic properties. The agreement between the values of discontinuities, calcd. from these equations, and the exptl. values testifies to the correctness of the assumptions made. The exptl. evidence showed that jumps at the intersection of these demarcation lines at the crit. point are finite in values. The demarcation line near the crit. point is then a parabola, the crit. isotherm is a 3rd-order curve, and its 1st deriv., which is not equal to 0, is a 2nd derivative. At the final jump value of the demarcation line, in the vicinity of the crit. point, no horizontal sections of finite dimensions can exist, as shown by the Mayer theory (G. Mayer and M. Hoppert-Mayer, *Statistical Mechanics* (1952)). The 2-phase equil. terminates at the crit. point, where the coexisting phases become identical, and the

KRIGHEVSKIY, T. R., KILNE, D. H. E.

crit. point is really a point, and not a whole existence range. Regardless of the jumps, the intersection of the demarcation line, and the intersection of the phase transition curves of the 2nd order are substantially different. The Gibbs equation, which characterizes the crit. phase as such, cannot characterize the 2nd-order phase-transition point. As a general conclusion, the classical theory of critical phenomena is confirmed.

W. M. Sternberg

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LFH

KRICHEVSKIY, I. R.

USSR/ Physical Chemistry - Thermodynamics. Thermochemistry. Equilibrium.  
Physicochemical analysis. Phase transitions

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Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11167

Author : Krichevskiy I.R.

Title : Reply to the Article by V.P. Skripov and V.K. Semchenko  
"Phase Transitions of Second Kind and Critical Phenomena. V. On Heat  
Capacity Maximum in Critical Region of Stratification of Binary  
Liquid Systems".

Orig Pub : Zh. fiz. khimii, 1955, 29, No 12, 2256-2260

Abstract : Discussion article. See RZhKhim, 1956, 18737

Card 1/1

Krichevskiy, I. R.

USSR/Chemistry - Physical chemistry

Card 1/1 Pub. 22 - 34/60

Authors : Krichevskiy, I. R.; Khazanova, N. Ye.; and Linshits, L. R.

Title : Critical phenomena in the triethylamine-water system

Periodical : Dok. AN SSSR 100/4, 737-740, Feb 1, 1955

Abstract : Experiments showed that the specific heat jump (change) for the triethylamine-water system during its conversion from homogeneous into heterogeneous state has a certain finite value at the critical point. An unusual sensitivity of the system investigated even to carbon dioxide traces was observed during the study of its equilibrium. The existence of specific heat changes in the critical point of mono- and dicomponent system was determined from the classical theory of critical phenomena. Fourteen references: 5 USSR, 4 German, 2 USA, 1 Canadian and 2 French (1884-1954). Tables; graphs.

Institution : State Scientific Research and Planning Institute of the Nitrogen Industry

Presented by : Academician A. N. Frumkin, July 13, 1954

KRICHEVSKIY T R

USSR/Physical Chemistry. Thermodynamics. Thermochemistry. B-8  
Equilibrium. Physicochemical Analysis. Phase Transitions

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 5720

Author : Krichevskiy I.P., Khazanova N.Ye.

Title : Formation of Mists at High Pressures

Orig Pub : Zh. tekhn. fiziki, 1956, 26, No 2, 422-429

Abstract : A procedure has been worked out for isothermal creation of oversaturation during formation of mist at high pressures, which is based on utilization of the phenomenon of minimum solubility of liquid in gas. Included is a layout of a unit for the investigation of the conditions of mist formation at high pressures, and the procedure of utilizing it is described. Investigated were the systems benzene-nitrogen, methanol-nitrogen,  $\text{CCl}_4$ -nitrogen, at a pressure of  $\sim 900$  atm. There was attained a sharp lowering of critical oversaturation, in comparison with the atmospheric pressure, which is, qualitatively, in accord

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15.10.1957, 1. 51

USSR/Statistical Physics - Thermodynamics.

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Abs Jour : Referat Zhur - Fizika, No 5, 1957, 11427

Author : Krichevskiy, I.R., Yefremova, G.D.

Inst : Institute of Nitrogen Industry, Moscow

Title : Setup With Visual Observation for the Investigation of  
Phase Equilibriums and Volume Relations in Gas and Liquid  
Systems.

Orig Pub : Zh. fiz. khimii, 1956, 30, No 8, 1877-1879

Abstract : A setup is described, which permits an investigation of the  
phase equilibriums and volume relations in gas and liquid  
systems, and in particular, permits determination of the  
solubility of liquids in liquids, of the compressibility  
of liquid and gas systems, and an investigation of the cri-  
tical phenomena in liquid-gas systems and liquid-liquid  
systems. The working space is the internal cavity

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USSR/Statistical Physics - Thermodynamics

D-3

Abs Jour : Ref Zhur - Fizika, No 5, 1957, 11427

(diameter 4 -- 5 mm) of a thick-wall glass tube, open on both ends. The upper and lower ends of the tubes are filled with mercury. Measurements of the mercury levels (or of the liquid levels) are carried out visually. The construction makes it possible to carry out investigations at pressures up to 100 -- 120 atmos.

Card 2/2

*KRICHEVSKIY, I. R.*

USSR/Statistical Physics - Liquids

D-8

Abs Jour : Referat Zhur - Fizika, No 5, 1957, 11521

Author : Krichevskiy, I.R., Tsekhanskaya, Yu.V.

Inst : Institute of Nitrogen Industry, Moscow.

Title : Diffusion and Dissolution in Liquid Solution in the  
Critical Region.

Orig Pub : Zh. fiz. khimii, 1956, 30, No 10, 2315-2326

Abstract : On the basis of the investigation performed on the influence of the critical region on the diffusion in a system comprising water and tri-ethyl-amine, a general conclusion is reached that the speed of diffusion in the critical region of a double system is very small and drops down to zero at the very critical point. Also investigated was the influence of the critical region on the kinetics of the heterogenous reaction. It is indicated, that in the

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USSR/Statistical Physics - Liquids

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Abs Jour : Ref Zhur - Fizika, No 5, 1957, 11521

critical regions of multi-component systems, the conclusions made remain approximately valid for the first and second components, provided their concentrations are large compared with the concentrations of the individual components.

Bibliography, 36 titles.

Card 2/2

*PROPERTY: L.R*

AUTHORS: Krichevskiy, I.R., Khazanova, N.Ye., Linshits, L.P. 76-12-16/27

TITLE: Liquid-Vapor-Equilibrium in the Benzene-Methanol-System at High Pressures (Ravnovesiye zhidkost'-par v sisteme-benzol-metanol pri vysokikh davleniyakh).

PERIODICAL: Zhurnal Fizicheskoy Khimii, 1957, Vol. 31, Nr 12, pp.2710-2716 (USSR)

ABSTRACT: The limiting curves of the liquid-vapor-equilibrium in the system of benzene-methanol at various compositions and temperatures from 150° C up to the critical temperature were investigated by means of the method of soldered ampules. The volumes of the benzene-methanol-system were measured at the limiting curves of the liquid-vapor-equilibrium. The investigated mixtures contained 16.7, 34.9, 50.6, 63.4 and 83.1 percentage by weight of benzene. The critical temperatures and volume-values were found for each of these mixtures and the critical t-x- and v-t curves were drawn. v - is the molar volume of the mixture of a given composition, x - benzene content in percentage by weight. The critical t-x-curve has a minimum which is observed with systems with steadily boiling mixtures under maximum vapor-pressure. These systems usually have such a minimum at the vapor-phase-line of the v-x-limiting curves. It is shown that the limiting curves occupy the whole range of the composition of the mixture at tempera-

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Liquid-Vapor-Equilibrium in the Benzene-Methanol-System  
at High Pressures

76-12-16/27

tures below the temperature of the minimum at the critical curve (238.5) and that with all temperatures for which diagrams were plotted, they have minima at the vapor-phase-line. At temperatures above the temperature-minimum at the critical curve, the limiting curves embrace only a part of the compositions adjacent to the axis of pure benzene and show critical points. It is shown that in the v-x-diagram for the benzene-methanol-diagram at 240° C (critical temperature of methanol) only one field of the heterogeneous equilibrium was determined, instead of the two expected. In the case of a further increase of temperature, this field embraces the reducing interval of composition. The minima at the vapor-phase-line of the v-x-limiting curves indicate the presence of azeotropes in the system. The composition of the minimum coincides with that below the maximum vapor-pressure only then, if and when the vapor-phase follows the laws of the ideal gases. It was assumed that the investigated mixture follows these laws and moreover the data available in literature on the composition of azeotrope mixtures were applied for this system at temperatures up to 131° C [Ref. 7]. The curves for the dependence of

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Liquid-Vapor-Equilibrium in the Benzene-Methanol-System  
at High Pressures

76-12-16/27

the boiling temperature of the azeotrope on its composition were drawn upon these bases. At a benzene content of 17 percentages by weight, and  $238.5^{\circ}\text{C}$  the t-x-curve of the azeotrope attains the critical t-x-curve immediately in the proximity of the minimum point. The data P-v-t for the benzene-methanol-system in reference 1, and the here obtained data for computing the pressures at equilibrium for three mixture-compositions were applied and the critical P-x- and P-t-curves were drawn. The P-v-limiting curves for the three mixtures were constructed from the here obtained data for the volumes of the phases with the investigated system at the limiting curve at various temperatures and compositions, as well as according to the data of reference 1. (Mixtures with 54.9, 70.9 and 83.0 percentage by weight of benzene at  $150^{\circ}$ ,  $200^{\circ}$ ,  $250^{\circ}$  and  $300^{\circ}\text{C}$ ). The critical P-t-curve was drawn according to the values for the critical parameters of pure benzene, methanol, and the three mixtures, as well as according to the data on the temperature-minimum at the critical curve for this system. This curve differs from those described in the references 8 and 9. It is shown that with the benzene-methanol-system the relation set up there is not observed: the component with

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Liquid-Vapor-Equilibrium in the Benzene-Methanol-System  
at High Pressures

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the least critical temperature (methanol) has the highest critical pressure. On the other hand, benzene shows at higher critical temperatures the lowest critical pressure. Finally, also the P-x-isotherms for the liquid-phase at 150° to 220° C, and isotherms for the liquid- and vapor phase at 240° and 250° C were constructed. There are 8 figures, 2 tables, and 9 references, 2 of which are Slavic.

ASSOCIATION: Institute of Nitrogen Industry, Moscow (Institut azotnoy promyshlennosti, Moskva).

SUBMITTED: September 17, 1956

AVAILABLE: Library of Congress

Card 4/4

AUTHOR KRICHEVSKIY I.R., YEFRENOVA G.D., LEONT'YEVA G.G. PA - 2760  
 TITLE On thermal stability of complexes formed by urea with organic compounds.  
 (O termicheskoy ustoychivosti kompleksov mocheviny s organicheskimi veshchestvami. - Russian)  
 PERIODICAL Doklady Akademii Nauk SSSR 1957, Vol 113, Nr 4, pp 817-819 (U.S.S.R.)  
 Received: 6/1957 Reviewed: 6/1957  
 ABSTRACT Urea forms crystalline complexes with nearly all types of organic compounds that have a straight chain: hydrocarbons, ethers, aldehydes, acids, alcohols, etc. The opinion prevails that at temperatures of more than 132.7°, i.e. at the melting point of urea, these complexes cannot exist. Although no such complexes have hitherto been discovered, it is nevertheless unexplainable from a thermodynamic point of view why 132.7° should be the upper limit for the existence of such a complex. Thermal constancy increases with the length of the chain of organic compounds. The thermal constancy of a complex obtained from a mixture of organic substances is higher than that which is due to individual compounds forming a mixture. On their search for complexes that are constant at temperatures of more than 132.7°

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PA - 2760

On thermal stability of complexes formed by urea with organic compounds.

the authors therefore carried out experiments with paraffin and ceresin, i.e. with multicomponent mixtures consisting on the whole of long-chain hydrocarbons of the paraffin series. They were synthesized with urea in a sealed glass tube. The urea complexes with ceresin of different types are constant at temperatures that are higher than the melting point of urea (up to  $141^{\circ}$  in the case of ceresin Nr. 3). This constancy could also be checked by studying the equilibrium between the complex and urea in unsaturated solutions of the latter. In aqueous solutions the thermal stability of the complex is dependent on the concentration of urea in the solutions. In order to be able to judge the constancy of the complex at temperatures of more than  $132,7^{\circ}$  it would be necessary to follow the course of the temperature curve. As a solvent liquid ammonia was used, as water is not suited for the purpose. The complex was synthesized in a manner similar to that described above. The temperature curve with paraffin ends at  $124,5^{\circ}$ , whereas the ceresin curve exceeds the melting point of

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PA - 2760

On thermal stability of complexes formed by urea with compounds.

urea and tends towards  $141,0^{\circ}$  (see above). Furthermore, the complex with cetane was investigated, where urea probably partly decays, and where the curve of solubility intersects the constancy curve of the complex at  $99^{\circ}$ . Besides, some qualitative observations concerning the forming of the complex were made. Thus it was shown by the examples of urea complexes with ceresin that the melting point of urea ( $132,7^{\circ}$ ) by no means forms a limit for the existence of this complex, but that it is constant up to  $141^{\circ}$ .

ASSOCIATION: State Scientific Research- and Projecting Institute for the Nitrogen Industry.

PRESENTED BY: A.N. FRUMKIN, member of the Academy.

SUBMITTED: 28.11. 1956

AVAILABLE: Library of Congress.

CARD 3/3

AUTHORS: Krichevskiy, I. R. Tsiklis, D. S. SOV/76-32-6-33/46

TITLE: Discussion (Diskussiya)  
Answer to the Paper by V. Yu. Urbakh "Is There a Finite Mutual Solubility of Gases?" (Otvét na stat'yu V. Yu. Urbakha "Sushchestvuyet li ogranichennaya vzaimnaya rastvorimost' gazov ?")

PERIODICAL: Zhurnal fizicheskoy khimii, 1958, Vol. 32, Nr 6, pp. 1407-1409 (USSR)

ABSTRACT: It is pointed out that already Kamerlingh Onnes and Keesom (Ref 1) laid down a theory on the equilibrium gas-gas, besides, corresponding notes are to be found in the book by Van der Waals-Konstamm (Ref 2). The main argument mentioned by Urbakh was mentioned by Batelli in 1892, it was, however, refuted as may be seen from the paper by A. G. Stoletov (Ref 3). The assumptions by A. Eucken (Ref 4) are explained by the theory of the phase transitions by L. D. Landau (Ref 6), while the statements by A. Ye., Sheyndlin (Ref 5) were again refuted by A.M. Rozen (Ref 7). In the further considerations contrary to the ideas by Urbakh the papers by Vogel (Ref 8), D. P. Konovalov (Ref 9) and I. R.

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Discussion. Answer to the Paper by V.Yu. SOV/76-32-6-33/46  
Urbakh "Is There a Finite Mutual Solubility of Gases?"

Krichevskiy and N. Ye Khazanova (Ref 10) are mentioned and it is found that for reasoning his assumption Urbakh had to develop a new theory in the place of the Gibbs-Stoletov theory, as otherwise the statement of a certain role played by surface phenomena in the thermodynamics of critical phenomena is without any scientific value and of no importance, just as the second assumption concerning the possibility of a lengthening of the curve of equilibrium liquid-gas beyond the critical point was refuted in the above mentioned papers. There are 10 references, 5 of which are Soviet.

ASSOCIATION: Institut azotnoy promyshlennosti, Moskva  
(Moscow, Institute of Nitrogen Industry)

SUBMITTED: November 11, 1957

1. Gases--Solubility
2. Gases--Theory
3. Gases--Phase studies
4. Gases--Thermodynamic properties

Card 2/2

AUTHORS: Krichevskiy, I. R., Sorina, G. A. SOV/76-32-9-20/46

TITLE: Phase and Volume Relationships in Liquid-Gas Systems Under High Pressure (Fazovyye i ob'yemnyye sootnosheniya v sistemakh zhidkost'-gaz pri vysokikh davleniyakh) VI. The System Cyclohexane-Hydrogen (VI. Sistema tsiklogeksan-vodorod)

PERIODICAL: Zhurnal fizicheskoy khimii, 1958, Vol 32, Nr 9, pp 2080 - 2086 (USSR)

ABSTRACT: The authors investigated the equilibrium in the cyclohexane-hydrogen system under a pressure of 700 atm. and at temperatures of 20°, 40°, and 60° C. The method used is described in reference 1, and the apparatus is represented in figure 1. The following quantities were measured: the solubility of hydrogen in cyclohexane (Table 1), the solubility of cyclohexane in hydrogen (Table 2), the molar volume of saturated solutions of hydrogen in cyclohexane (Table 3), and the molar volume of unsaturated solutions of hydrogen in cyclohexane (Table 4). The evaluation of the results in graphs (Figs 2, 3, and 4) shows that the solubility of the investigated

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Phase and Volume Relationships in Liquid-Gas Systems Under High Pressure. VI. The System Cyclohexane-Hydrogen SOV/76-32-9-26/46

system is described by the equation of Krichevskiy-Il'inskaya (Refs 1,11,13). The authors thank G.D.Yefremova for her advice, and G.G.Leont'yeva for her assistance in carrying out a series of experiments. There are 4 figures, 6 tables, and 16 references, 12 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy institut azotnoy promyshlennosti, Moskva (Moscow Scientific Research Institute for the Nitrogen Industry)

SUBMITTED: April 2, 1957

Card 2/2

AUTHORS: Krichevskiy, I. R., Khazanova, N. Ye., 20-119-5-37/59  
Linshits, L. R.

TITLE: Diffusion Within the Critical Range of Ternary Solutions  
(Diffuziya v kriticheskoy oblasti troynykh rastvorov)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 119, Nr 5,  
pp. 975-977 (USSR)

ABSTRACT: The aim of the present work is restricted to the solution of the main problem, namely the clear determination of the problem, whether a noticeable enrichment of the solution with the third component occurs (playing the part of a small addition to the binary system) in the critical range because of molecular diffusion. The investigation of the diffusion in ternary solutions was for various reasons carried out by the example of the trimethylamine-water system with an addition of a small amount of butylamine. The investigation was carried out by means of the method of capillaries (about  $\sim 2$  mm diameter and about  $\sim 40$  mm length). The experimental lasted 50-90 hours. The thermal stabilizing was accurate

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Diffusion Within the Critical Range of Ternary Solutions

20-119-5-37/59

to an error of  $\pm 0,05^{\circ}\text{C}$ . The investigation of the diffusion in the ternary mixture is always carried out with solutions of the same ratio butylamine: triethylamine (about  $\sim 1:14$ ), and always at the same temperature of  $18^{\circ}\text{C}$ . In order to reach exact results a great gradient of the concentrations of the diffusing component was selected for the investigations. The following can be seen from the data mentioned in 2 tables: The diffusion coefficient of the butylamine is of the same order within the critical range and in diluted solutions. The little smaller value of the diffusion coefficient in diluted solutions is explained by their small viscosity as compared to concentrated solutions. Thus the diffusion velocity of butylamine does not decrease within the critical range while the diffusion velocity of triethylamine within this range strongly decreases. However, diluted solutions the diffusion coefficient of triethylamine has the same order as the diffusion coefficient of butylamine. According to the theoretical conditions the system was enriched with butylamine. The ratio butylamine: 1 : 6,

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Diffusion Within the Critical Range of Ternary Solutions

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while in the original mixture it was 1 : 14. Thus the first investigation of the diffusion velocity within the critical range of ternary solutions shows, in agreement with theory, the possibility of the enrichment of the solution with the third component by molecular diffusion. There are 2 tables and 4 references, 3 of which are Soviet.

ASSOCIATION: Gosudarstvenny nauchno-issledovatel'skiy i proyektnyy institut azotnoy promyshlennosti  
(State Scientific Research and Planning Institute of Nitrogen Industry)

PRESENTED: December 24, 1957, by A. N. Frumkin, Member, Academy of Sciences, USSR  
SUBMITTED: December 21, 1957

Card 3/3



5(4)

AUTHORS:

Krichevskiy, I. R., Tsekhanskaya, Yu. V.

SOV/20-122-2-25/42

TITLE:

The Convective Diffusion in Liquid Solutions Under Turbulent Conditions (Konvektivnaya diffuziya v zhidkikh rastvorakh pri turbulentnom rezhime)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 2, pp 258-259 (USSR)

ABSTRACT:

V. G. Levich set up the following equation of the convective diffusion in liquid solutions to the surface of a rotating disk under turbulent conditions:

$$I \sim \frac{0,01 c_0 s}{\alpha \text{Pr}^{3/4}} (a \omega) \left( \frac{\nu}{a^2 \omega} \right)^{1/5}$$

I denotes the diffusion flux (potok), s - the area of the disk, a - the radius of the disk, c<sub>0</sub> - the concentration of the substance in the core (yadro) of the solution, ω - the angular velocity of the rotating disk, ν - the kinematic viscosity of the solution, α - a universal constant. This paper deals with the experimental confirmation of the above

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SOV/20-122-2-25/42

The Convective Diffusion in Liquid Solutions Under Turbulent Conditions

given equation and with the finding of the numerical value of  $\alpha$ . For the experimental proof of the above mentioned equation, the authors measured the velocity of the dissolution of terephthalic acid (which is practically water-insoluble) in diluted aqueous solutions such as water-triethylamine, water-hexaethylamine, and water-ammonia according to the method of the rotating disk under turbulent conditions. The apparatus for the measurements and the experimental method were discussed in a previous paper (Ref 8). A table gives the results of the measurements of the diffusion fluxes together with all the data necessary for the calculation of the value of  $\alpha$ . The errors of the determination of the diffusion fluxes under turbulent conditions amounted to 3-6 %. For  $\alpha$ , the average value 0,13 was found. The probable error of a single measurement of  $\alpha$  was equal to  $\pm 0,01$  and the probable error of the average value of  $\alpha$  amounted to  $\pm 0.003$ . Thus, the value of  $\alpha$  does not depend on the nature of the diffusing substance. The constancy of the value of  $\alpha$  confirms the assumptions of L. D. Landau and V. G. Levich concerning the nature of the turbulent motion in liquids near a solid surface. There are 1 table and 10 references, 7 of which are Soviet.

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The Convective Diffusion in Liquid Solutions Under Turbulent Conditions

SOV/20-122-2-25/42

ASSOCIATION: Nauchno-issledovatel'skiy i proyektnyy institut azotnoy  
promyshlennosti  
(Scientific Research and Planning Institute of the Nitrogen  
Industry)

PRESENTED: May 8, 1958, by S. I. Vol'fkovich, Academician

SUBMITTED: May 7, 1958

Card 3/3

SOV/20-122-3-21/57

AUTHORS: Krichevskiy, I. R., Ivanovskiy, G. F., Safronov, Ye. K.

TITLE: The Solubility of Silicon Tetraiodide in Nonaqueous Solvents:  
(Rastvorimost' tetrayodida kremniya v nevodnykh rastveritel'nykh)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 3, pp 400-402  
(USSR)

ABSTRACT: The recrystallization of the substance mentioned first in the title in nonaqueous solvents is one of the important stages of the purification of the first and serves for the production of highly pure silicon. Since only a limited number of publications dealt with this problem (Refs 1,2) the authors prepared the following paper. As solvents were used: benzene, toluene, xylene, cyclohexane, chloroform, normal octane and silicon tetrachloride. The solubility was determined according to the Alekseyev method (Ref 3). Constant temperatures were kept by means of an oil-thermostat. The mixture was stirred at temperatures close to those of the disappearance of the solid phase. This was enough for the establishment of the equilibrium between the liquid and the solid phase. The curves of solubility are shown on figure 1. The results obtained strongly deviate from data given in

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The Solubility of Silicon Tetraiodide in Nonaqueous Solvents

SOV/20-122-3-21/57

publications (Ref 2). Obviously the latter may be regarded as wrong. It can be supposed from the character of the curves that the solutions investigated are regular. There are 1 figure, 1 table, and 7 references, 1 of which is Soviet.

PRESENTED: May 9, 1958, by S. A. Vekshinskiy, Member, Academy of Sciences, USSR

SUBMITTED: April 25, 1958

Card 2/2

KRICHEVSKIY, I. R.

28(8)  
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 307 459  
 Akademiya nauk SSSR, Otdeleniye khimicheskikh nauk  
 Termodinamika i stroeniye rastvorov: trudy soveshchaniya...  
 (Thermodynamics and Structure of Solutions; Transactions of the  
 Conference Held January 27-30, 1958) Moscow, Izd-vo AN SSSR,  
 1959. 255 p. 3,000 copies printed.  
 Ed.: M. I. Shakhparov, Doctor of Chemical Sciences; Ed. of Publishing  
 House: M. O. Yegorov; Tech. Ed.: T. V. Polyakova.  
 PURPOSE: This book is intended for physicists, chemists, and  
 chemical engineers.

COVERAGE: This collection of papers was originally presented at the  
 Conference on Thermodynamics and Structure of Solutions sponsored  
 by the Section of Chemical Sciences of the Academy of Sciences,  
 USSR, and the Department of Chemistry of Moscow State University,  
 and held in Moscow on January 27-30, 1958. Officers of the  
 Academy are listed in the Foreword. A list of other reports  
 presented at the conference, but not included in this book,  
 is also given. Among the problems treated in this book are:  
 electrolytic solutions, ultrasonic measurements, spectro-  
 scopic analysis, etc. References accompany individual articles.

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KRICHEVSKIY, I. R. (Moscow)

"Thermodynamik der Systeme bei hohen und höchsten Drucken."

report submitted for the Symposium on Reactions at Ultra-High Pressure, IUPAC,  
31 August-1 Sept 1959.

5(4)

SOV/76-33-5-30/33

AUTHORS:

Krichevskiy, I. R., Sorina, G. A. (Moscow)

TITLE:

The Polythermal Method of the Investigation of Phase Equilibria Liquid - Gas at High Pressure and Temperatures (Politermicheskiy metod issledovaniya fazovykh ravnovesiy zhidkost' - gaz pri vysokikh davleniyakh i temperaturakh)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 5, pp 1151 - 1153 (USSR)

ABSTRACT:

The method described was tested with the system cyclohexane - carbon dioxide. The measurement consists of two processes: during the first process the components are fused into a glass tube, heated in a thermostat, and then the temperature is measured at which one phase disappears. The diagrams for two dependences are obtained from the system  $v - t - N$ , and from them the diagram for the third dependence is plotted. The pressure-temperature dependence is measured in a metallic ampulla provided with a manometer. The dependence  $p - N$  for  $t = \text{const.}$  is also found graphically. There are 5 figures and 2 references, 1 of which is Soviet.

ASSOCIATION: Institut azotnoy promyshlennosti (Institute of Nitrogen Industry)

SUBMITTED: September 5, 1958  
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S/170/60/003/010/020/023x  
B019/B054

AUTHORS: Krichevskiy, I. R., Khazanova, N. Ye., Linshits, L. R.

TITLE: Diffusion of Gases Near the Critical Point

PERIODICAL: Inzhenerno-fizicheskiy zhurnal, 1960, Vol. 3, No. 10,  
pp. 117-118

TEXT: In the introduction, the authors point out that it is very difficult to investigate the molecular diffusion of gases near the critical point. They observed visually the diffusion of iodine in carbon dioxide. Iodine pressed into tablets and carbon dioxide were introduced into thick-walled glass ampoules. The diffusion of iodine in carbon dioxide causes a discoloration of carbon dioxide, and thus the diffusion of iodine in liquid and gaseous carbon dioxide was investigated. In this way, a diffusion coefficient of  $1 \cdot 10^{-5} \text{ cm}^2/\text{sec}$  at  $20^\circ \text{C}$  was determined in liquid carbonic acid. From the results obtained, the authors conclude that the diffusion coefficient near the critical point is smaller than  $1 \cdot 10^{-6} \text{ cm}^2/\text{sec}$ , and that the diffusion coefficient near the critical

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Diffusion of Gases Near the Critical Point

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B012/B054

point is reduced by at least three orders of magnitude. There are 4 references: 2 Soviet and 2 Scandinavian.

ASSOCIATION: Gosudarstvennyy institut azotnoy promyshlennosti,  
g. Moskva  
(State Institute of the Nitrogen Industry, Moscow)

SUBMITTED: April 18, 1960

Card 2/2

5 (4)

AUTHORS:

Krichevskiy, I. R., Yefremova, G. D.

SOV/76-33-6-25/44

TITLE:

Phase Equilibria in the Melamine-ammonia System (Fazovyye ravnovesiya v sisteme melamin - ammiak)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 6, pp 1328-1335 (USSR)

ABSTRACT:

An interesting case of phase equilibrium (PE) in binary systems is the one where the critical curve and the solubility curve intersect (Ref 1). In both intersecting points P and Q, critical phenomena can be observed in saturated solutions in the presence of the solid phase B<sub>(solid)</sub> (Fig 1). The described (PE) occurs if the melting point of one component B lies considerably above the critical temperature (CT) of the other component A, and the solubility B<sub>(solid)</sub> in A<sub>(liqu)</sub> is low and decreases with the temperature. In such systems, there are two areas of pressure and temperature in which the three-phase equilibrium (TPE) of solid body - liquid - gas can be observed. Between these two areas, there is the area of two-phase equilibrium (TPE') of solid body - gas. The above-mentioned equilibrium is to be found in the melamine-ammonia system. Is there is a

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Phase Equilibria in the Melamine-ammonia System

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considerable difference between the (CT) of ammonia (I) and the melting temperature of melamine (II); the (PE) was investigated by 3 different methods: In sealed glass ampules, by the dynamic method and by the inflexion of the pressure-temperature curves. The (TPE) of solid (II) - solution of (I) in liquid (II) - solution of (II) in gaseous (I), which occurs above the (CT) of (I), was studied by the last-mentioned investigation method (Fig 2 shows the device used). The (TPE') of solid (II) - gaseous solution was examined on a device designed by D. S. Tsiklis (Fig 4); the solubility and density of the solid (II) in gaseous (I) was measured at temperatures of 150-300° C and a pressure of 200-500 atmospheres. At the (CT) of the solution of solid (II) in liquid (I) (134° C), critical phenomena could be observed in the presence of solid (II). The second critical point of the equilibrium liquid - gas in the presence of solid (II) was determined:  $P \approx 700$  atm,  $t \approx 245^\circ\text{C}$  at a content of  $\approx 50\%$  by weight of (II). Data on the solubility of (II) in (I) (Table 1), on the (CT) of the solution of (II) in liquid (I) (Table 2), on the (TPE) of the system (II) - (I) (Table 3), on the solubility of solid (II) in gaseous (I), and on the density of these solutions (Table 5),

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Phase Equilibria in the Melamine-ammonia System

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as well as a space diagram drawn according to the data obtained of the (PE) of the system (II) - (I) (Fig 5), are presented. Finally, the authors express their thanks to D. S. Tsiklis, G. G. Leont'yeva, M. T. Filipov and R. O. Keroleva. There are 5 figures, 5 tables, and 11 references, 4 of which are Soviet.

ASSOCIATION: Gosudarstvennyy institut azotnoy promyshlennosti (State Institute of Nitrogen Industry)

SUBMITTED: October 25, 1957

Card 3/3

3 (4)

AUTHORS:

Krichevskiy, I. R.; Khazanova, N. Ye., SCV/76-33-7-7/40  
Tsekhanskaya, Yu. V.; Linshits L. R.

TITLE:

Critical Phenomena in the System Hexamethylene Imine - Water.  
I. Equilibrium Limiting Curve of Liquid - Liquid Near the  
Critical Point

PERIODICAL:

Zhurnal fizicheskoy khimii, 1959 Vol 33, Nr 7, pp 1484 - 1491  
(USSR)

ABSTRACT:

From the data of the classical theory on the critical phenomena new thermodynamic relations can be obtained (Refs 1-3) which combine the course of the limiting curve (LC) near the critical point (CP) with the jumps of the derivatives of some properties during the transition of the system from the homogeneous to the heterogeneous state. In previous papers (Refs 4-9) it was found for two systems by the method of the jump of the derivative  $(\partial v / \partial t)_{p,x}$  of the course of the (LC) near the critical point

that the limiting curves of these systems are second-degree parabolas. In continuation of these investigations the authors analyzed the system hexamethylene imine (I) - water (II). They investigated the course of the (LC) (Fig 1, Table 1) near the

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Critical Phenomena in the System Hexamethylene  
Imine - Water. I. Equilibrium Limiting Curve of  
Liquid - Liquid Near the Critical Point

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(CP), the partial and total vapor pressure, the specific weight, the refractive index, the viscosity, and the diffusion coefficients within the wide range of temperature and composition. Investigations were carried out near the lower (CP) at 66.9°C and 22.5 wt% (I) by means of a gravimetric dilatometer (Refs 11-14) (Fig 1) which was contained in a thermostat. The authors investigated six systems with a hexamethylene imine content of 13.7, 20.1, 24.32, 27.6, 31.4, and 35.6 wt% at various temperatures (Table 2). On the basis of the results of the specific volumes, volume-temperature curves were plotted, and herefrom the authors calculated the derivatives  $(\partial v/\partial t)_{P,x}$  on the (LC) for the heterogeneous and the homogeneous range as well as the jumps of the derivatives at the point of intersection of the (LC). Results showed that the jump of the derivative  $(\partial v/\partial t)_{P,x}$  attains a limit in the critical point, and thus the (LC) is a second-degree parabola near the (CP). In (Refs 18-20), the jumps of  $c_{P,x}$  and  $(\partial v/\partial t)_{P,x}$  of some binary solutions and

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Critical Phenomena in the System Hexamethylene  
Imine - Water. I. Equilibrium Limiting Curve of  
Liquid - Liquid Near the Critical Point

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the jumps of  $c_v$  of several pure substances were investigated, and it was found that these jumps always attain limits in the (CP). It is therefore assumed that the (LC) of the liquid - liquid and of the liquid - vapor in the systems under investigation is a second-degree parabola near the (CP). There are 5 figures, 2 tables, and 21 references, 14 of which are Soviet.

ASSOCIATION: Gosudarstvennyy institut azotnoy promyshlennosti (State Institute for Nitrogen Industry)

SUBMITTED: September 11, 1957

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SOV/76-33-10-34/45

5(4)

AUTHORS: Krichevskiy, I. R., Tsekanskaya, Yu. V.

TITLE: Dissolution of Solid Acids in Binary Liquid Solutions in the Critical Range

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 10, pp 2331 - 2338 (USSR)

ABSTRACT: This paper deals with the influence exercised by the critical range on the kinetics of heterogeneous processes which take place under different hydrodynamic conditions. The rate of dissolution of terephthalic acid in the systems triethylamine - water at 17° and hexamethylenimine - water at 30, 40, and 67.5° was determined under laminar and turbulent conditions as well as the rate of dissolution of adipic, sebacic, and salicylic acid in the system triethylamine - water at 17° and under laminar conditions. Exact data on the experimental methods are given. Experiments with laminar flows led to two observations: 1) The experimental values of dilute solutions are in agreement with those computed according to equation (1) for convective diffusion towards the surface of a rotating disk by V. G. Levich (Ref 7); 2) for increasing triethylamine and hexamethylenimine

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Dissolution of Solid Acids in Binary Liquid Solutions  
in the Critical Range

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concentration and approximation to the critical composition, the rate of dissolution of the various solid acids is equal in the same solution. The computations of the diffusion flows carried out by Yu. B. Ivanov and V. G. Levich (Ref 8) are in good agreement with the present experimental data. For turbulent flows L. D. Landau (Ref 9) and V. G. Levich (Ref 10) assumed that the convection of the substance in the layer took place immediately at the surface of the solid (where the chemical reaction proceeded) due to turbulent pulsations, whereas L. Prandtl (Ref 11) and G. Karman (Ref 12) (Abstracter's note: Karman's first name is written in the text with G., in the bibliography with T.) assume a laminar flow without pulsations in this layer. From the experimental data obtained the universal constant was computed here from equation (2) by Levich for the convective diffusion towards the surface of the rotating disk in turbulent flows (Table). The constant value of the universal constant confirm Levich's theory and the afore-mentioned assumption by Landau and Levich. Experiments on the dissolution in binary mixtures of liquids without critical point (ammonia + water) showed that also in this case the rate of the heterogeneous chemical reaction may be

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Dissolution of Solid Acids in Binary Liquid Solutions  
in the Critical Range

independent of the composition of the solution if the removal  
of the reaction products determines the reaction rate. There  
are 8 figures, 1 table, and 14 references, 10 of which are Soviet.

ASSOCIATION: Institut azotnoy promyshlennosti, Moskva (Institute of Nitrogen  
Industry, Moscow)

SUBMITTED: March 31, 1958

Card 3/3

KRITICHESKIY I R

30

PHASE I BOOK EXPLOITATION SOV/5469

Soveshchaniye po kriticheskim yavleniyam i flyuktuatsiyam v rastvorakh. Moscow, 1960.

Kriticheskiye yavleniya i flyuktuatsii v rastvorakh; trudy soveshchaniya, yanvar' 1960 g. (Critical Phenomena and Fluctuations in Solutions; Transactions of the Conference, January 1960) Moscow, Izd-vo AN SSSR, 1960. 190 p. 2,500 copies printed.

Sponsoring Agencies: Akademiya nauk SSSR. Otdeleniye khimicheskikh nauk. Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova. Khimicheskii fakul'tet.

Responsible Ed.: M. I. Shakhparonov, Doctor of Chemical Sciences, Professor; Ed. of Publishing House: E. S. Dragunov; Tech. Ed.: S. G. Tikhomirova.

PURPOSE : This collection of articles is intended for scientific personnel concerned with chemistry, physics, and heat power engineering.

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# Critical Phenomena and Fluctuations

COVERAGE: The book contains 24 of the 26 reports read at the Conference on Critical Phenomena and Fluctuations in Solutions organized by the Chemical Division of Moscow State University, January 26-28, 1960. The reports contain results of investigations carried out in recent years by Soviet physicists, chemists, and heat power engineers. The Organizing Committee of the Conference was composed of Professor Kh. I. Amirkhanov, A. Z. Golik, I. R. Krichevskiy (Chairman), V. K. Samenchenko, A. V. Storonkin, I. Z. Fisher, and M. I. Shaldparonov (Deputy Chairman). References accompany individual articles.

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skiy oblastnoy pedagogicheskoy institut -- Pedagogical Insti-  
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Rott, L. A. [Minskiy lesotekhnicheskoy institut -- Minsk  
Forestry Engineering Institute]. Concerning the Diffusion in  
the Critical Stratification Region

102

Card 6/9

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Critical Phenomena and Fluctuations

30V/5469

Roshchina, G. P. [Laboratoriya molekulyarnoy fiziki, Fizicheskiy fakul'tet, Kiyevskiy gosudarstvennyy universitet im. T. G. Shevchenko -- Laboratory of Molecular Physics, Division of Physics, Kiyev State University imeni T. G. Shevchenko] Investigation of Fluctuations in Solutions by the Method of Light Scattering

109

Skipov, V. P. [Laboratoriya molekulyarnoy fiziki, Ural'skiy politekhnicheskiy institut im. S. M. Kirova -- Laboratory of Molecular Physics, Ural Polytechnic Institute imeni S. M. Kirov]. Special Structural Features of Matter in the Vicinity of the Critical Point and Transfer Phenomena

117

Skipov, V. P., and Yu. D. Kolpakov [Laboratory of Molecular Physics, Ural Polytechnic Institute imeni S. M. Kirov, and the Laboratoriya teplofiziki, Ural'skiy filial AN SSSR -- Thermophysics Laboratory, Ural Branch, AS USSR]. Light Scattering in Carbon Dioxide along Pre- and Post-Critical Isotherms

126

Smirnov, B. A. [Institut neftekhimicheskogo sinteza AN SSSR -- Card 7/9

30

|  |          |     |
|--|----------|-----|
| Critical Phenomena and Fluctuations  | SOV/5469 |     |
| Institute of Petrochemical Synthesis, AS USSR (Moscow)] Visual Observations in the Critical Region   |          | 137 |
| Fisher, I. Z., and V. K. Prokhorenko. Concerning the Fluctuations of Coordination Numbers in Liquids   |          | 142 |
| Fisher, I. Z. [Belorusskiy Gosudarstvennyy Universitet -- Belorussian State University (Minsk)] Correlation Analysis of the Critical Point   |          | 148 |
| Shakhmarov, M. I. [Laboratory of the Physical Chemistry of Solutions, Chemistry Division, Moscow State University imeni M. V. Lomonosov]. Fluctuations in Solutions  |          | 151 |
| Shimanskaya, Ye. T., and A. Z. Golik [Laboratory of Molecular Physics, Physics Division, Kiev State University imeni T. G. Shevchenko]. Investigation of the Critical State, Liquid-Vapor, of Solutions by Tepler's Method |          | 161 |

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3c

Critical Phenomena and Fluctuations

SCV/5469

Shimanskaya, Ye. T., Yu. I. Shimanskiy, and A. Z. Golik [Laboratory of Molecular Physics, Division of Physics, Kiev State University imeni T. G. Shevchenko]. Investigation of the Critical State of Pure Substances by Tepler's Method

171

Resolution of the Conference on Critical Phenomena and Fluctuations in Solutions

189

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JZ/dfk/jw  
10-28-61

Card 9/9

S/030/60/000/05/38/056  
B015/B008

AUTHORS: Krichevskiy, I. R., Doctor of Chemical Sciences,  
Shakhparonov, M. I., Doctor of Chemical Sciences

TITLE: Critical Phenomena and Fluctuations in Solutions

PERIODICAL: Vestnik Akademii nauk SSSR, 1960, No. 5, pp. 96-99

TEXT: A Conference on the above mentioned problems, which was convened by the Otdeleniye khimicheskikh nauk Akademii nauk SSSR (Department of Chemical Sciences of the Academy of Sciences USSR) and the khimicheskii fakul'tet Moskovskogo universiteta (Chemical Department of Moscow University), was held from January 26 to 28, 1960. It was attended by approximately 150 physicists and physicochemists from various cities of the Soviet Union. The reports dealt with the thermodynamics of critical phenomena, the statistical theory of the solutions in the critical range, the thermodynamics of irreversible processes in the critical range, the fluctuations in solutions, and other problems. A. Z. Golik, Yu. I. Shimanskiy, and Ye. T. Shimanskaya (Kiyev) reported on investigations of the critical state of pure materials and solutions according to Tepler's method. ✓

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Critical Phenomena and Fluctuations in  
Solutions

S/030/60/000/05/38/056  
B015/B008

I. R. Krichevskiy, N. Ye. Khazanova, and L. R. Linshits investigated the dependence of the chemical potentials of the components of binary and ternary systems of compound and temperature. V. P. Skripov and Yu. D. Kolpakov (Sverdlovsk) reported on the investigation results of light dispersion in the supercritical region of carbon dioxide. I. R. Krichevskiy and N. Ye. Khazanova referred to problems of the diffusion in liquid and gas solutions near the critical point. L. A. Rott (Minsk) reported on the theory of diffusion near the critical point of separation into layers. V. P. Skripov explained the course of viscosity near the critical point on the basis of a "Colloid Model". I. R. Krichevskiy and Yu. V. Tsakhanskaya reported on the investigation of convective diffusion. D. K. Beridze described the investigation results of light dispersion in the range of the critical point of the separation into layers of the solutions nitrobenzene - hexane, nitrobenzene - heptane and methyl alcohol - cyclohexane. V. F. Mordukhai reported on investigations with ultrasonic in liquids near the critical point. After a discussion on the critical state, the Conference came to the conclusion that there is no reason at present to reject the classic thermodynamic theory of the critical phenomena, developed by Gibbs, A. G. Stoletov, and other authors. M. I. Shakhparonov reported

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Critical Phenomena and Fluctuations in  
Solutions

S/030/60/000/05/38/056  
B015/B008


on the main results of his investigations in the field of the theory of fine-structure fluctuations with a small particle content. N. N. Lomova, M. I. Shakhparonov, R. M. Kasimov, and Ya. Yu. Akhadov reported on the results of experimental investigations of dielectric properties of solutions. L. V. Lashina mentioned measurement results of the fine structure of light dispersion in acetone - water- and water - methyl alcohol solutions. M. F. Vuks and L. I. Lisnyanskiy (Leningrad) conducted investigations of fluctuation phenomena in the solutions of pyridine and  $\alpha$ -picoline in water, as well as of pyridine in alcohols. G. P. Roshchina (Kiyev) mentioned data of experimental investigations of light dispersion in solutions, as well as of the conclusions on the dependence of fluctuations on composition, temperature and type of the molecules of the solution components. L. P. Zatsepina reported on the light dispersion in individual liquids and solutions with photoelectric measurements, and established in this connection the conformance with the theory by Einstein-Smolukhovskiy. N. V. Mokhov, Ya. M. Labkovskiy, and I. V. Kirsh (Dnepropetrovsk) reported on their investigations of fluctuations of density in ether and benzene, as well as of fluctuations of concentration in carbon bisulfide - methyl alcohol solutions. The Conference confirmed

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Critical Phenomena and Fluctuations in  
Solutions

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the importance of the theoretical and experimental investigation of the molecular structure of the material in the range of the critical point. Organizational measures were decided upon for the further development of the scientific studies in the field of critical phenomena and fluctuations in solutions, as well as for their application to scientific-economic problems. It was decided further to conduct periodic seminars in Moscow on problems of the theory of the liquid state and the theory of solutions. The 2nd All-Union Conference on the Theory of Solutions is to be convened in 1962.



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Krichevskiy, I. R.

(6)

3/078/60/005/05/35/037  
SC04/2016

AUTHORS: Yananayev, I. V., Lushnaya, N. P.

TITLE: The XVII Congress on Pure and Applied Chemistry

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 3, pp. 1178 - 1183

TEXT: The XVII Congress of the IUPAC (International Union of Pure and Applied Chemistry) took place in Munich from July 30 to September 6, 1959. It was preceded by the IX Conference of the IUPAC (August 26-29, 1959) which was attended by a Soviet delegation consisting of B. A. Kazanskii (re-elected as representative of the USSR at the Bureau of the IUPAC), M. M. Shevarkin (elected as a member of the Section of Organic Chemistry), A. P. Vinogradov (elected as Deputy Chairman of the Section of Geochemistry), I. V. Yananayev (elected as a member of the Section of Inorganic Chemistry), Ya. I. Gerasimov, O. A. Reutov, and G. I. Batsaninov. Further, I. P. Alimarin was appointed Second Secretary of the Section of Analytical Chemistry. About 1200 delegates attended the Congress. In a plenary session O. A. Reutov delivered a lecture: "The Mechanism of the Formation of Metal-Carbon Bond and Some Considerations on the Reactivity of Organometallic Compounds of Heavy Metals". Concerning the work of the sections the

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following is reported: Section I (Organometallic Compounds): 66 lectures. A report on the work of this section will be given later on. Section II (Chemistry of Actinides): 36 lectures. Section III (Chemistry of Actinides and Lanthanides): 31 lectures, among them D. I. Ryabchikov: "Complex Formation of Rare Earths and I. V. Yananayev: "On the Composition of Ferrous Cyanides of the Rare Earths and Titanium". Section IV (Fluorine Chemistry): 21 lectures. Section V (Preparation of Pure Metals): 16 lectures. Section VI (Non-aqueous Solvents): 16 lectures. Section VII (Homogeneous and Heterogeneous Gas Equilibria): 9 lectures. Section VIII (Semiconductors and Non-metallic Compounds): 24 lectures. Section IX (Ternary Oxides and Sulfides): 35 lectures, among them N. P. Lushnaya: "The Phase Diagram of the Ternary System  $\text{CaO} - \text{P}_2\text{O}_5 - \text{SiO}_2$ ". Section X (Various Communications): 101 lectures, among them Ya. K. Delenarskiy (Kiev): "Polarography of Melted Salts", L. F. Levin (Riga): "On the Kinetics of Exchange Reactions Between Metals and Water", and Ya. I. Gerasimov: "Thermodynamic Properties of Iron- and Cobalt Antimonides". Reactions at ultrahigh pressures were dealt with at a symposium. I. R. Krichevskiy reported on: "Thermodynamics of Systems at High and Supercritical Pressures".

Card 2/2

KRICHEVSKIY, I.R.; KHAZANOVA, N.Ye.; TSEKHANSKAYA, Yu.V. (Moscow)

Critical phenomena in the system hexamethylenimine -  
water. Part 3: Diffusion in the vicinity of the criti-  
cal point. Zhur.fiz.khim. 34 no.6:1250-1254 Je '60.  
(MIRA 13:7)

1. Institut azotnoy promyshlennosti.  
(Hexamethylenimine) (Diffusion) (Critical point)

KRICHEVSKIY, I.R.; SORINA, G.A.

Liquid - gas phase equilibria in the systems cyclohexane - carbon dioxide and cyclohexane - nitrous oxide. Zhur. fiz.khim. 34 no.7:1420-1424 J1 '60. (MIRA 13:7)

1. Institut azotnoy promyshlennosti, Moskva.  
(Cyclohexane) (Carbon dioxide) (Nitrogen oxide)  
(Phase rule and equilibrium)

S/076/60/034/008/018/C39/XX  
B015/B063

AUTHORS: Krichevskiy, I. R., Khazanova, N. Ye., Smirnov, L. P.

TITLE: Critical Phenomena in the Hexamethylenimine - Water System.  
IV. Total Vapor Pressure

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 8,  
pp. 1702 - 1705

TEXT: The critical isotherm of total pressure above binary solutions like the isotherms of the chemical potential and partial pressure, exhibits an almost horizontal section in which the vapor pressure is practically independent of the composition of the solution. This effect of the critical point also extends to the homogeneous region, in a wide range of composition and temperature. The authors studied the thermodynamics of binary solutions near the critical point in the hexamethylenimine - water system, which has its lower critical point at  $68.1^{\circ}\text{C}$  and 24.8 percent by weight of hexamethylenimine (Ref.2). In doing so, they measured the total vapor pressure above the solutions with 5-55 percent by weight of hexamethylenimine from  $40^{\circ}$  to  $74^{\circ}\text{C}$  by the isothermoscope method. The latter has

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Critical Phenomena in the Hexamethylenimine - S/076/60/034/008/018/039/XX  
Water System. IV. Total Vapor Pressure B015/B063

been developed by Smith and Mensies (J. Amer. Chem. Soc., 32, 1412, 1910) and is described here. Both instrument and method were checked by determining the vapor pressure of bidistilled water. The measurement error of the total vapor pressure above solutions of different compositions is indicated as being 0.10 - 0.20 mm Hg. The values obtained from the diagram  $\log P = f(1/T)$  were interpolated for integral temperature values and tabulated (Table 1). From this the  $P = f(x)$  diagram was drawn and the limiting curve was plotted therein, the data on the liquid - liquid equilibrium in the system concerned being derived from Ref. 2. The  $P = f(x)$  diagram (Fig. 3) shows that the effect of the critical point extends over a wide range of temperature and composition. A thermodynamic interpretation of the data given here will be offered in a later report. There are 3 figures, 2 tables, and 4 references: 2 Soviet, 1 US, and 1 German.

ASSOCIATION: Institut azotnoy promyshlennosti Moskva (Institute of the Nitrogen Industry, Moscow)

SUBMITTED: September 26, 1958

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S/076/60/034/008/018/039/XI  
3015/3063

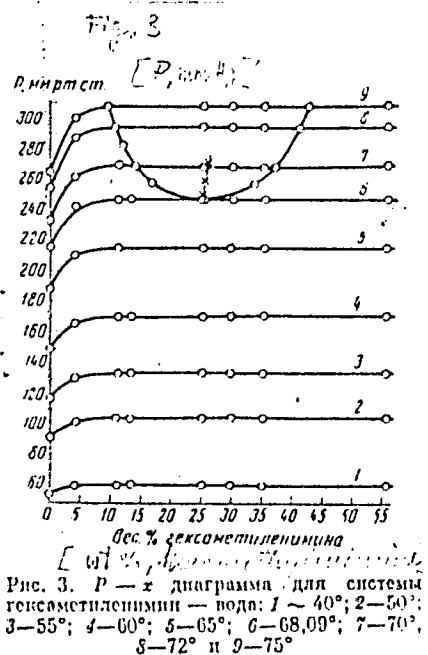
*Table 1*

Таблица 1

Общее давление пара над растворами гексаметиленмина (ГМН) в воде, мм рт. ст.  
(интерполированные данные)

| Состав,<br>вс. %<br>ГМН | Температура, °C |       |       |       |       |       |       |       |       |
|-------------------------|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|
|                         | 40              | 50    | 55    | 60    | 65    | 69,1  | 70    | 72    | 73    |
| 5                       | 60,2            | 102,2 | 131,2 | 167,1 | 211,0 | 242,7 | 265,2 | 290,1 | 304,2 |
| 10                      | 60,9            | 104,0 | 133,3 | 169,1 | 214,3 | 246,8 | 269,0 | 294,1 |       |
| 15                      | 61,0            | 104,1 | 133,5 | 170,0 | 214,8 | 247,5 |       |       |       |
| 20                      | 61,0            | 104,2 | 133,6 | 170,1 | 214,9 | 247,6 |       |       |       |
| 25                      | 61,1            | 104,2 | 133,6 | 170,2 | 215,0 | 247,6 | 269,1 | 294,6 | 308,5 |
| 30                      | 61,1            | 104,3 | 133,7 | 170,3 | 215,1 | 247,6 |       |       |       |
| 35                      | 61,2            | 104,3 | 133,8 | 170,4 | 215,2 | 247,7 |       |       |       |
| 40                      | 61,2            | 104,4 | 133,9 | 170,5 | 215,3 | 247,9 | 269,3 |       |       |
| 45                      | 61,3            | 104,5 | 134,0 | 170,6 | 215,4 | 248,1 | 269,3 | 294,9 | 308,6 |
| 50                      | 61,3            | 104,6 | 134,1 | 170,7 | 215,5 | 248,2 | 270,1 | 295,2 | 308,8 |
| 55                      | 61,4            | 104,7 | 134,2 | 170,8 | 215,6 | 248,3 | 270,3 | 295,4 | 308,9 |

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B015/B063

Text to figure and table:

Fig. 3 - P-x diagram for the hexamethylenimine - water system: 1 - 40°C, 2 - 50°C, 3 - 55°C, 4 - 60°C, 5 - 65°C, 6 - 68.09°C, 7 - 70°C, 8 - 72°C, 9 - 75°C;

Table 1 - Total Vapor Pressure Above the Solutions of Hexamethylenimine (HMI) in Water, mm Hg (interpolated values),

1 - Composition, wt% HMI;  
2 - Temperature, °C.

S/076/60/034/009/025/041XX  
B020/B056

AUTHORS: Krichevskiy, I. R., Khazanova, N. Ye., and Linshits, L. R.  
TITLE: Critical Phenomena in the System Hexamethylene Imine - Water.  
V. Partial Pressures of the Components  
PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 9,  
pp. 1920 - 1927



TEXT: For the purpose of explaining the characteristics of the behavior of a substance in the critical point and the effect produced by these characteristics upon the behavior of a substance near the critical point, it is first necessary to determine the dependence of the chemical potential of the component upon the composition of the mixture in these regions. For the temperature dependence of the differentials of isothermal and isobaric lines upon the partial pressures of the components from the composition in the critical point of the binary solution the equations

$$\left[ \left( \frac{\partial}{\partial T} \right) \left( \frac{\partial P_1}{\partial N_2} \right)_{P,T} \right]_{P,N_2,k} = \left[ (P_{1,k} N_{2,k}) / (RT_k^2) \right] \left[ \left( \frac{\partial^2 H}{\partial N_2^2} \right)_{P,T,k} \right] \quad (26) \text{ and}$$

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Critical Phenomena in the System Hexamethylene Imine - Water. V. Partial Pressures of the Components S/076/60/034/009/025/041XX B020/B056 ✓

$$\left[ \left( \frac{\partial}{\partial T} \right) \left( \frac{\partial P_2}{\partial N_2} \right)_{P,T} \right]_{P,N_2,k} = - \left[ \left( P_{2,k} \frac{N_{1,k}}{RT_k^2} \right) \cdot \left( \frac{\partial^2 H}{\partial N_2^2} \right) \right]_{P,T,k} \quad (27)$$

are derived, where  $k$  is the index of the critical phase. The partial pressures of the components in the critical range of the binary solution were investigated in the system hexamethylene imine - water with a lower critical point at  $68.1^\circ$  and 24.8 % by weight of hexamethylene imine (Ref. 5). The investigation was carried out by means of the dynamic method, where only the equilibrium composition of the liquid and of the vapor was determined. The total vapor pressure over the solutions was separately determined (Ref. 6). The equilibrium is established only slowly near the critical point of a binary system, and therefore particular care was taken in order that the saturators be used effectively. Helium was the carrier gas. A scheme of the arrangement is given in Fig. 1. The equilibrium in the system hexamethylene imine - water was measured in solutions with five different compositions at  $50.0$ ,  $62.1$ , and  $67.6^\circ$ . From the equilibrium compositions of the vapor- and liquid phases, the partial pressures of the components were determined (the partial pressures of hexamethylene imine

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Critical Phenomena in the System Hexamethylene Imine - Water. V. Partial Pressures of the Components S/076/60/034/009/025/041XX  
B020/B056

are given in Fig. 2). The proportionality of the partial pressure of the components with concentration holds only for diluted solutions (with 3 - 4% by weight of hexamethylene imine). At temperatures near critical one, the partial pressure of hexamethylene imine from a concentration of about 8% onward remains constant within a broad range of compositions. At 50°, the partial pressure within the range of this composition increases somewhat with concentration, but its dependence of composition remains very low, which fully corresponds to the conditions given in the thermodynamic equations (26) and (27). In solution concentrations near the critical one, the composition of the gaseous phase changes only little with temperature. The temperature dependence  $p_2/p_1$  for three ternary systems is shown in

Fig. 3: triethyl amine - water, phenol - water, and hexamethylene imine - water, from which it may be seen that this function converges to zero when approaching the critical temperature. Between evaporation and the solution heats of the components at the critical point, a relation is obtained, which does not follow from the general thermodynamics of the critical state, namely

$$\Delta H_{1, ev} - \Delta H_{2, ev} = \Delta H_{1, k, sol} - \Delta H_{2, k, sol}$$

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Critical Phenomena in the System Hexamethylene S/076/60/034/009/025/041XX  
Imine - Water. V. Partial Pressures of the B020/B056  
Components

There are 3 figures, 1 table, and 9 references: 6 Soviet, 1 US, and  
2 German.

ASSOCIATION: Gosudarstvennyy institut azotnoy promyshlennosti, Moskva  
(State Institute of the Nitrogen Industry, Moscow)

SUBMITTED: November 12, 1958

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84625

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54210

2209, 1273 only

S/076/60/034/010/002/022

B015/B064

AUTHORS: Krichevskiy, I. R., Khazanova, N. Ye., Svetlova, G. M.  
(Deceased), and Panina, R. S.

TITLE: Total Vapor Pressure Over the Solutions of Triethyl  
Amine - Water in the Critical Range

PERIODICAL: Zhurnal fizicheskoy khimii, 1960. Vol. 34 No. 10.  
pp. 2160 - 2166

TEXT: Investigations of the total vapor pressure over binary solutions in the vicinity of the critical point are interesting for two reasons. On the one hand, it is important to establish according to which laws a distribution of the critical phenomena in the homogeneous region takes place, on the other hand, it is important to study the problem of jumps of the intensive quantities when intersecting the limiting curve both in the critical point and at a distance from it; the importance of this has already been stressed by the authors of the present paper (Ref. 1). For the mentioned reasons the authors

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Total Vapor Pressure Over the  
Solutions of Triethyl Amine -  
Water in the Critical Range

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B015/B064

investigated the critical parameters for the equilibrium liquid -  
liquid in the system triethyl amine - water. For this purpose special-  
ly purified triethyl amine was used (specific weight at  
25°C = 0.72345 g/cm<sup>3</sup>, refractive index at 25°C  $n_D = 1.398$ ).

The vapor pressure of triethyl amine was determined (Table 3) and the  
total pressure of vapor over the system triethyl amine - water in the  
temperature range of from 10° to 25°C (Fig. 2) and the limiting curve  
for the equilibrium of the system investigated, i.e. the critical  
solution temperature (Table 4, Fig. 1). As may be seen from Fig. 2  
the isosteric curve of the solution with a composition close to that  
of the critical (30.56 wt% triethyl amine) passes continuously over  
into the limiting curve, while the curves for the solutions with  
different compositions form an angle with the equilibrium curve. The  
experimental values and the calculated ones show that the derivation  
of the values of the total pressure according to temperature

$$(\partial P_{\text{total}} / \partial T)_{N_2}$$

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Total Vapor Pressure Over the  
Solutions of Triethyl Amine -  
Water in the Critical Range

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as well as the derivations of the other intensive values show no jump on intersecting the limiting curve at the critical point. This coincidence of the experimental and calculated data confirms the accuracy of the theoretical assumptions. From Diagram  $\log P = f(1/T)$  (Fig. 2) the values for the total pressure over the solution were interpolated for integral values of temperature (Table 5), the P - x diagram plotted (Fig. 3), the limiting curve drawn, and thus, the values of the vapor pressures on the boundary line obtained (Table 6). Fig. 3 shows that at concentrations close to the critical point a slight dependence of the total vapor pressure over the solutions on the concentration is to be observed in the wide temperature range. This corresponds fully to the thermodynamic characteristics of the behavior of substances in the vicinity of the critical point. D. Mayer and V. F. Alekseyev are mentioned. There are 3 figures, 6 tables, and 11 references: 7 Soviet, 2 British, 1 German, 1 French.

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| 1<br>Темпера-<br>тура, °C | 2<br>Давление,<br>мм рт. ст. | 3<br>Темпера-<br>тура, °C | 4<br>Давление,<br>мм рт. ст. |
|---------------------------|------------------------------|---------------------------|------------------------------|
| 13,58                     | 36,7                         | 40,55                     | 135,1                        |
| 18,07                     | 48,5                         | 60,25                     | 292,5                        |
| 23,50                     | 62,8                         | 70,12                     | 555,15                       |
| 27,57                     | 76,6                         | 80,4*                     | 760*                         |
| 32,20                     | 94,0                         |                           |                              |

S/076/60/034/010/002/022  
B015/B064

| 1<br>Концентрация<br>триэтиламина,<br>% вес | 2<br>Темпера-<br>тура,<br>°C | 3<br>Давление,<br>мм рт.<br>ст. | 4<br>Концен-<br>трация<br>триэтила-<br>мина,<br>% вес | 5<br>Темпера-<br>тура,<br>°C | 6<br>Давление,<br>мм рт.<br>ст. |
|---|------------------------------|---------------------------------|---|------------------------------|---------------------------------|
| 7,7   | 24,0                         | 78,7                            | 18,0  | 18,6                         | 57,2                            |
| 8,9   | 22,0                         | 70,4                            | 23,2  | 18,4                         | 56,8                            |
| 11,4  | 20,0                         | 62,0                            | 30,0  | 18,35                        | 56,7                            |
| 15,1  | 19,0                         | 59,0                            | 32,2*   | 18,33*                       | 56,6*                           |

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Table 5

| Концентрация триэтил-амин. % вод. | 12°  | 15°  | 17°  | 18,33°* | 20°    | 22°    | 24°    |
|-----------------------------------|------|------|------|---------|--------|--------|--------|
| 5,0                               | 23,8 | 31,9 | 37,7 | 42,3    | 49,5   | 57,5   | 66,8   |
| 10,0                              | 33,5 | 42,6 | 49,0 | 54,5    | 61,6   |        |        |
| 15,0                              | 38,1 | 45,4 | 52,1 | 56,5    | 62,6** | 70,4** | 78,7** |
| 20,0                              | 38,8 | 45,5 | 52,1 | 56,6    | 62,6   | 70,4   | 78,7   |
| 25,0                              | 38,9 | 45,6 | 52,1 | 56,6    | 62,6   | 70,4   | 78,7   |
| 30,0                              | 37,2 | 45,0 | 52,1 | 56,6    | 62,6   | 70,4   | 78,7   |
| 32,0                              | 37,3 | 45,7 | 52,1 | 56,6    | 62,6   | 70,4   | 78,7   |

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B015/B064

Fig. 35

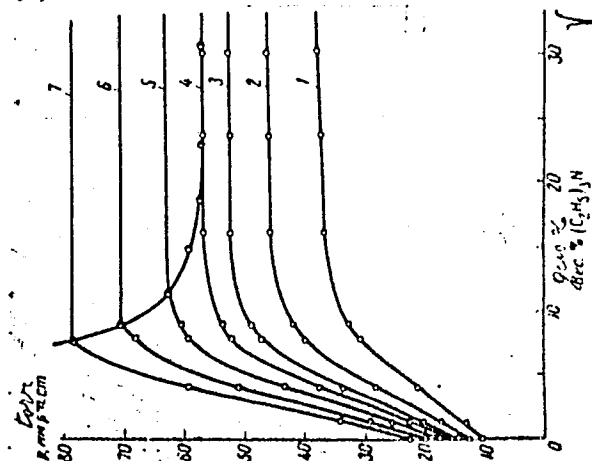


Рис. 3. Диаграмма  $P-x$  в системе триэтил-  
амин — вода. 1 — 12°, 2 — 15°, 3 — 17°,  
4 — 18,33°, 5 — 20°, 6 — 22°, 7 — 24°

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Total Vapor Pressure Over the  
Solutions of Triethyl Amine - Water  
in the Critical Range

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B015/B064

Legend to figures and tables : Fig. 3, P - x diagram in the system  
triethyl amine - water. 1 - 12°C, 2 - 15°C, 3 - 17°C, 4 - 18.33°C  
5 - 20°C, 6 - 22°C, 7 - 24°C; Table 3, vapor pressure of pure triethyl  
amine, 1 = temperature, °C, 2 = pressure in mm Hg, 3 = temperature,  
°C, 4 = pressure in mm Hg; Table 5, total vapor pressure over the  
solutions triethyl amine - water (interpolated values), in mm Hg: 1 =  
= concentration of triethyl amine in wt%, 2 = 18.33 critical tempera-  
ture of unmixing, xx = values under the horizontal lines referring  
to the heterogeneous region; Table 6, vapor pressure over the solutions  
triethyl amine - water on the limiting curve of the equilibrium  
liquid - liquid, 1 = concentration of triethyl amine in wt%,  
2 = temperature, °C, 3 = pressure in mm Hg. X

ASSOCIATION: Institut azotnoy promyshlennosti Moskva  
(Institute of the Nitrogen Industry Moscow)

SUBMITTED: November 12, 1958

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182143-10

KRICHV. IV, I.M.; YAKUBOVA G.D.; PEZAKOVA, R.O.; POLYAKOV, Ye.V.

Phase and volume relations in the system acetic acid-  
nitro. Zhur. pri. kh. 7:44, 1961. (HRA 14:7)  
(acetic acid)  
(nitro)

20641  
S/020/61/136/006/017/024  
B101/B203

5.4400(1273, 1274, 1372)

AUTHORS: Krichevskiy, I. R. and Rott, L. A.

TITLE: The theory of the Brown motion in the critical range

PERIODICAL: Doklady Akademii nauk SSSR, v. 136, no. 6, 1961, 1368-1371

TEXT: Proceeding from earlier papers (Refs. 1-3), the authors study the vanishing of the Brown motion in the critical range when a mixture is separated into two layers. For the mean square displacement of the particle, they write down:  $S^2 = 2Dt$  (1). As  $D$  is a diffusion coefficient, it must vanish in the critical range as was experimentally proved in Ref. 4 on iodine dissolved in  $CO_2$ . The present paper interprets this standstill of the particle. The authors proceed from Smolukhovskiy's equation:

$$\omega(t_0, \bar{R}_0; t + \tau, \bar{R}) = \int \omega(t_0, \bar{R}_0; t, \bar{r}) \omega(t, \bar{r}; t + \tau, \bar{R}) d\bar{r}, \quad (2),$$

where  $\omega$  is the probability density for that the particle passes over from

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The theory of the Brown motion in the...

state  $\bar{R}_0$  into state  $\bar{r}$  in the time  $t - t_0$ . In the critical range, this does no longer take place in a homogeneous medium. This is explained with the aid of a one-dimensional example. The possibility of displacement of a particle along a straight line in the form of a series of steps of two types is discussed. Any displacement may occur to the right or to the left. For steps of the same type, the probability is  $1/2$ . It is assumed that  $N$  steps of the second type correspond to a distance  $L$ . The probability of continuous displacement to the right by the distance  $l < L$  is calculated. Proceeding from Poisson's law  $f_\lambda(n)$ , where  $\lambda = Nl/L$ ,  $m > n$ ,  $n \gg 1$  ( $m$  = steps of the first type,  $n$  = steps of the second type), the authors write down for the probability:

$$P_l = \sum_n f_\lambda(n) \sum_{\beta=0}^n \sum_{\gamma=0}^{[n/2]} \varphi(n) (1/2)^{m+n-2\gamma-2\beta} (p_1 p_2)^{\beta+\gamma} \quad (\beta \leq n - 2\gamma). \quad (4)$$

$\varphi(n)$  is the probability for that  $n$  steps correspond to the distance  $l$ .  $\gamma$  is the number of groups with at least two steps of the second type,  $\beta$  is the number of single steps adjoining at least two steps of the opposite type.

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$$\varphi(n) = \left\{ 1 + \sum_{\gamma=1}^{n/2} (n-2\gamma+1) \right\}^{-1} \quad (5)$$

holds for this case. After summation in equation (4), the following is obtained:

$$P_1 = \sum_n f_\lambda(n) \varphi(n) \frac{1 - (4\rho_1\rho_2)^n [2 + 1/2n - 16(1/2n+1)\rho_1^2\rho_2^2]}{2^{m+n} (1 - 4\rho_1\rho_2)^2 (1 + 4\rho_1\rho_2)} \quad (6)$$

For the case  $\gamma = 0$ , the following is written down:

$$P_{11} = \sum_n f_\lambda(n) (1/2)^{m-n} \rho_1^2 \rho_2^n \quad (7)$$

It is attempted to attain agreement of these derivations with the real motion of a particle by equating the steps of the first type to steps in dense volume sections, and those of the second type to steps in places

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The theory of the Brown motion in the...

of low density. In this case, (4) corresponds to a motion in a homogeneous medium, (7) to a motion in the critical state.  $p_2$  is the probability for a passage of the particle from an elementary volume of higher to one of lower density:  $p_2 > 1/2$ . A comparison of probabilities (6) and (7) gives  $P_I \gg P_{II}$ . The problem is generally formulated by Markov's method (Ref. 7). (2) is transformed, the change in density being considered:

$$\omega(t_0, \bar{R}_0, \rho_0; t + \tau, \bar{R}, \rho_R) = \int \omega(t_0, \bar{R}_0, \rho_0; t, \bar{r}, \rho_r) \omega(t, \bar{r}, \rho_r; t + \tau, \bar{R}, \rho_R) d\bar{r} d\rho_r, \quad (8),$$

where  $Q_r = q(\bar{r})$  is the density. The function  $\omega$  is expanded in a series, only the first two terms of which are used; equation (8) is multiplied by the distribution function  $f(Q_0, Q_R)$ , and by integration over the entire volume the following is obtained:

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$$\begin{aligned} & \int \omega(t_0, \bar{R}_0, p_0; t + \tau, \bar{R}, p_R) f(p_0, p_R) dV dp_0 dp_R = \\ & = \int \omega_{0r}(p_{kp}, p_r) \omega_{rR}(p_{kp}, p_R) f(p_0, p_R) d\bar{r} dV dp_0 dp_r dp_R + \dots \\ & \dots + \int \left. \frac{\partial \omega_{0r}}{\partial p_0} \right|_{p_{kp}} \left. \frac{\partial \omega_{rR}}{\partial p_R} \right|_{p_{kp}} (p_0 - p_{kp})(p_R - p_{kp}) f(p_0, p_R) d\bar{r} dV dp_0 dp_r dp_R. \quad (10) \end{aligned}$$

The following is written down as a general form of (10):

$$A = B + C \int_V (\epsilon_0 - \epsilon_{crit})(\epsilon_R - \epsilon_{crit}) dV \quad (11). \quad \text{A discussion of these}$$

equations leads to the conclusion that the probability density for the displacement of a Brown particle vanishes near the critical point. In this range, (1) does no longer hold since  $\overline{S_1 S_2} \neq 0$  in an inhomogeneous medium and, therefore, a function  $f(t) = f(t_1) + f(t-t_1)$ , on which (1) was based, can no longer be derived. The study of the behavior of Brown

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The theory of the Brown motion in the...

particles offers new possibilities for studying microscopic relaxation processes. There are 8 Soviet-bloc references.

ASSOCIATION: Gosudarstvennyy nauchno-issledovatel'skiy i proyektnyy institut azotnoy promyshlennosti i produktov organicheskogo sinteza (State Scientific Research and Planning Institute of the Nitrogen Industry and Products of Organic Synthesis)

PRESENTED: September 19, 1960, by A. N. Frumkin, Academician

SUBMITTED: September 16, 1960

Card 6/6

KRICHEVSKIY, I.R.; KHAZANOVA, N.Ye.; LINSHTS, I.R.

Iodine diffusion in compressed carbon dioxide near the critical point. Dokl. AN SSSR 141 no.2:397-399 N '61. (MIRA 14:11)

1. Gosudarstvennyy nauchno-issledovatel'skiy i proyektnyy institut azotnoy promyshlennosti i produktov organicheskogo sinteza.  
Predstavleno akademikom S.I.Vol'fkovichem.  
(Iodine) (Carbon dioxide)

S/064/62/000/002/005/008  
B101/B144

inf. 4500

AUTHORS: Krichevskiy, I. R., Khazanova, N. Yo., Lesnevskaya, L. S.,  
Polyakova, Z. A.

TITLE: Diffusion in gases at high pressures

PERIODICAL: Khimicheskaya promyshlennost', no. 2, 1962, 29-35

TEXT: The diffusion in the  $N_2 - CO_2$  system under pressure was measured. The method consists in filling capillaries (8 mm diameter, 70 mm length) with purified  $CO_2$ , while  $N_2$  is in the chamber surrounding the capillaries. The gas mixture contained in the capillaries after diffusion is analyzed. To prevent convection, the capillaries are filled with silver wire netting, width of mesh 0.04 mm<sup>2</sup>. The diffusion coefficient calculated on the basis of Pick's equation was corrected, allowing for the apparatus constant 1.74, caused by filling with the net. The investigation was conducted at 25, 28.15 and 31.5°C and 6-74 atm. At 31.5°C,  $D_{N_2} \cdot 10^3$  cm<sup>2</sup>/sec amounted to:

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Diffusion in gases at high ...

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| Pressure<br>atm | molar part of N <sub>2</sub> |      |      |
|-----------------|------------------------------|------|------|
|                 | 0.25                         | 0.30 | 0.45 |
| 24.0            | 4.97                         | 5.03 | 6.10 |
| 47.0            | 2.03                         | 2.43 | 2.83 |
| 58.6            | 1.65                         | 2.00 | 2.37 |
| 70.0            | 0.90                         | 1.05 | 1.20 |
| 74.0            | 0.33                         | 0.43 | 0.53 |

A calculation of the diffusion coefficient on the basis of the Enskog-Chapman theory and its extension to gases by W. Jost, using the equation of state by I. R. Krichevskiy and Ya. S. Kazarnovskiy (ZhFKh, 13, 378 (1939)) and the constant by V. P. Markov (ZhFKh, 15, 410 (1941)) produced, up to 50 atm, a maximum deviation of 12%

between experiment and calculation. For higher pressures, there is a significant difference between experiment and theory. The absence of an exact diffusion theory caused the authors to start a series investigation of the diffusion in gases at high pressures. There are 6 figures, 2 tables, and 31 references: 7 Soviet and 24 non-Soviet. The four most recent references to English-language publications read as follows: Chan-Hue Chon, I. I. Martin, Ind. Eng. Chem., 49, 758 (1957); L. R. Mifflon, C. O. Bennett, J. Chem. Phys., 29, 975 (1958); H. H. Reamer, B. H. Sage, Transport Properties of Gases, Proc. Gas. Dynamics Symposium, 2-nd, Evanston, 1957, 62 (pub. 1958); Iigo Osugi, H. Hiraoka, D. Shinoda, Rev. Phys. Chem., 28, no. 1, 36 (1958).  
Card 2/2

X

KRICHEVSKIY, I.R.; KHAZANOVA, N.Ye.; LESNEVSKAYA, L.S.; POLYAKOVA, Z.A.

Diffusion in gases at high pressures. Khim.prom. no.2:105-111  
F '62. (MIRA 15:2)

(Diffusion)

KRICHEVSKIY, I.R.; KHAZANOVA, N.Ye.; LESNEVSKAYA, L.S.; SANDALOVA, L.Yu.

Equilibrium liquid - gas at high pressures in the nitrogen -  
carbon dioxide system. Khim.prom. no.3:169-171 Mr '62.

(MIRA 15:4)

(Nitrogen) (Carbon dioxide) (Phase rule and equilibrium)

33475

S/170/62/005/002/008/009  
B104/B138

24.5600

AUTHORS: Krichevskiy, L. R., Khazanova, N. Ye., Lesenevskaya, L. S.

TITLE: Fick's diffusion equation

PERIODICAL: Inzhenerno-fizicheskiy zhurnal, v. 5, no. 2, 1962, 101 - 103

TEXT: The system nitrogen - carbon dioxide has been studied in the light of Fick's equation near the critical point. At 15°C and 105 at, the volume is largely dependent on the composition in a certain range of concentrations (Fig. 1a). This dependence of volume on the molar fraction of the component results in a complex dependence between it and the volume concentration (Fig. 1b). In the section AB, the component diffuses from B to A, which requires a negative diffusion coefficient in Fick's equation  $dm/dt = -DSgradC$ , where  $m$  is the amount of substance diffusing in time  $t$ ,  $D$  is diffusion coefficient,  $S$  is the diffusion area, and  $C$  is the volume concentration of the diffusing substance. According to Fick's equation, the rate of diffusion should be zero at point A; however, since diffusion also takes place here, the diffusion coefficient would become infinitely great. These difficulties can be overcome by regarding not the gradient of volume

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S/170/62/005/002/008/009

B104/B138

Fick's diffusion equation

concentration, but that of the chemical potential, as the driving force of diffusion. Fick's equation can be used in spite of the complex dependence of molar volume on composition near the critical point. However, the results of investigation of molecular diffusion are extremely difficult to evaluate. The kind of concentration dependence of the molar volume near the critical point of the pure solvent, as described above, is a specific feature of all gas solutions. There are 1 figure and 4 Soviet references. U

ASSOCIATION: Institut azotnoy promyshlennosti i produktov organicheskogo sinteza, g. Moskva (Institute of the Nitrogen Industry and Products of Organic Synthesis, Moscow)

SUBMITTED: June 12, 1961

Card 2/3

KRICHEVSKIY, I.R.: TSEKHANSKAYA, Ye.V.

Photodissociation of iodine in carbon dioxide solutions under  
critical conditions. Inzh.-fiz.zhur. 5 no.12:104-107 D '62.  
(MIRA 16:2)

1. Nauchno-issledovatel'skiy i proyektnyy institut azotnoy  
promyshlennosti i produktov organicheskogo sinteza, Moskva.  
(Dissociation) (Iodine) (Carbon dioxide)

KRICHEVSKIY, I.R.; KHAZANOVA, N.Ye.; KAL'SINA, M.V.

Diffusion near the critical demixing point of the system  
triethylamine - water - phenol. Inzh.-fiz. zhur. 5  
no.6:93-96 fe '62. (MIRA 15:12)

1. Institut azotnoy promyshlennosti, Moskva.  
(Diffusion)  
(Systems (Chemistry))

S/862/62/002/000/015/029  
A059/A126

AUTHORS: Krichevskiy, I.R., Khazanova, N.Ye., Linshits, L.R.

TITLE: Diffusion in gases near the critical point of the liquid-vapor equilibrium

SOURCE: Teplo- i massoperenos. t. 2: Teplo- i massoperenos pri fazovykh i khimicheskikh prevrashcheniyakh. Ed. by A.V. Lykov and B.M. Smol'skiy. Minsk, Izd-vo AN BSSR, 1962. 132 - 135

TEXT: The diffusion in very diluted solutions near the critical point has been experimentally examined on the iodine-carbon dioxide system. It could be assumed that, due to the low solubility of iodine in  $\text{CO}_2$ , the critical parameters of the binary system will be close to those of pure  $\text{CO}_2$ , i.e.,  $t_c = 31.06^\circ\text{C}$ ,  $p_c = 72.9 \text{ atm}$ , and  $\rho_c = 0.467 \text{ g/cm}^3$ . The method used was based on the direct visual observation of the colored layer (brown in gaseous  $\text{CO}_2$  and violet in liquid  $\text{CO}_2$ ) containing iodine the velocity of motion of which was measured and the intensity compared with the standard. The error of the visual observation was 1.5 - 2 mm. Constant temperature was maintained with an accuracy of  $\pm 0.02^\circ\text{C}$ .

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